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Research

ZINC SULFIDE ANTI-REFLECTIVE THIN FILM COATING FOR GERMANIUM OPTICAL WINDOWS

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ABSTRACT

In this work, Anti-reflective thin film is made on Germanium (Ge) optical window, which is one of the most used materials in thermal imaging systems. ZnS material was used its optical transmittance between 2-14 μm and due to the fact that it has a refractive index proportional to the refractive index of Ge. ZnS thin films have been prepared by Radio Frequency (RF) magnetron sputtering on Germanium (Ge) optical windows for anti-reflection coating (ARC). ZnS films were produced at different thicknesses using RF sputtering system working pressures under 3, 20 and 30 mTorr. The other RF systems parameters such as RF power, deposition temperature were kept constant for all depositions. Crystal structures, optical and surface properties of ZnS thin films were characterized with X-ray diffraction (XRD), Atomic force microscopy (AFM), Fourier transform ınfrared (FTIR) and UV-VIS transmission spectrometer. The characterization results of Ge optical windows coated ZnS thin films grown at 3 mTorr pressure show that high optical transmission and good crystallinity in ınfrared wavelength region (2-14 μm).

Keywords: RF magnetron sputtering; Anti-reflective thin film; ZnS thin film, Growth parameters effect.

1. INTRODUCTION

Thin film anti-reflective coating is widely used the aim for fulfil or minimize reflections from the front and back surfaces of materials [1-4]. The increase in the permeability of the material with these coatings allows the improvement of optical properties. Unwanted reflection losses occur on the material surfaces, due to the high refractive index of the materials. For this reason, all nearly lens surfaces are given an antireflection coating to improve the light transmission and to eliminate detrimental effect [5-7].

Infrared transparent materials are gaining more and more importance every day especially night vision, remote sensing and communication. Germanium (Ge), one of these transparent materials, is the most commonly used material in infrared region as lens, optical windows, domes and optical filters due to its optical properties [8, 9]. The refractive index of single crystal Ge is about 4.00 (at 10 μm) and its reflection loss is approximately 50% in the wavelength range of 2-14 μm [8, 10, 11]. This unwanted reflection loss was occurred on the surface of its and reduces the optical efficiency [12, 13]. The optical transmission of Ge can have increased when AR coating is applied to the Ge's surface [14, 15]. Anti-reflection coating (ARC) for Ge lenses or optical windows is not only increased the optical transmission, but also provides surface adhesion, durability, protection and image clarity [4, 7, 16]. Material selection for ARC is one of the main problem in the desired wavelength range. The properties of many materials are not suitable for the ARC in infrared regions such as durability, toxicity, radioactivity, ect [17]. The other problem is the refractive index of the material. Particularly, ARC materials for the IR region must have both optical transmission and the refractive index must be proportional with the refractive index of Ge's. Considering these conditions, there is a limited number of coating materials.

It has been reported that single-sided, double-sided and multi-layer ARC can achieve high transmission by decreasing reflection between interfaces of air and materials. Especially with the integration of photovoltaic solar cells, ARC studies have gained a special importance. In solar cells, single layer ARC's such as MgF_2 (n=1.3 – 1.4) have been applied and short circuit current density value can improve. In order to achieve minimum reflection for infrared region imaging and other applications with low-cost, simple operation, Zinc sulfide (ZnS) was selected as anti-reflective coating material. ZnS is a semiconductor II-VI compound with refractive index of 2.20 and has an optical transmission of 0.4-13 μm [18]. This ensures that it is suitable as a transparent material in the visible and infrared regions. ZnS thin films can be produced into thin films using a variety of techniques such as thermal evaporation deposition, chemical bath deposition (CBD), electrochemical deposition, sol-gel, spin-coating or dip-coating, DC or RF magnetron sputtering etc [12, 18-22].
The thickness of the ZnS thin films is obtained for the Germanium using the Fresnel's equation [22].

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$$\boldsymbol{d} = \frac{\lambda}{4n_f} \quad (1)$$

in which n_f, are the refractive index of the ARC material and d is the thickness of the antireflection coating thin film, respectively. Single layer anti-reflective coatings exhibit maximum optical transmission for single wavelength, while multi layer anti-reflective coatings exhibit maximum optical transmission in the broad spectrum [23]. But for multi-layer antireflection, there are many difficulties affecting the characteristics of the film, such as the use of multiple materials, film production and stabilization to be optimized in appropriate thicknesses.

Herein, we prepared single layer, double layer and multi layer ZnS thin films as ARC on Ge optical window. The structural, optical and surface properties of ZnS anti-reflective thin films were investigated to some coating parameters. To depict the effect of pressure in ARC, single layer samples with the same thickness of multi-layer ARC properties have been conducted.

2. MATERIAL AND METHOD

Zinc sulfide (ZnS) thin films were fabricated on p-type Ge substrate by RF magnetron sputtering system. Ge were cleaned by ultrasonication bath for 15 min at 80°C bath temperature in deionized water and cleaned ethanol, acetone, respectively. After the cleaning process, the substrates were loaded into the RF magnetron system. ZnS with purity of 99,99% was used as target material for deposition into. The distance between the target and substrates were set up about 30 mm. Before deposition, sputtering system was evacuated to base pressure (≈10^{-6} Torr) and Ar gas with flow rate 30 sccm was introduced into the chamber. The substrate temperature was set up 100 °C and were grown under 100 W. ZnS antireflective thin films generated chosen film thicknesses under working pressures 3,10 and 20 mTorr.

After the deposition, the thicknesses of the ZnS films were determined by stylus type profilometer (Veeco, Dektak 150) and shown in Table 1 and Table 2. The structural properties of Ge optical windows with and without ZnS thin films were obtained by X-ray diffraction (XRD) technique using APD 2000 PRO diffractometer system. The optical transmission properties of ZnS thin films were measured by the Vertex 80 Fourier transform infrared spectrometer (FTIR) in wavelengths ranging from 2 to 20 µm. UV-VIS transmission measurement were taken using Perkin Elmer Lambda 2. The surface morphology of ZnS thin films were imaged with an atomic force microscopy (NanoMagnetics Instruments Ltd., Oxford, UK).

Table 1. The thickness of ZnS thin films on single surface

Sample (for 3-5 µm)	Pressure (mTorr)	Average Thickness (nm)	Sample (for 8-12 µm)	Pressure (mTorr)	Average Thickness (nm)
S1	3	429	**S13**	3	1166
S2	20	430	**S14**	3	1226
S3	30	421	-	-	-

Table 2. The thickness of ZnS thin films on double surface

Sample (for 3-5 µm)	Pressure (mTorr)				Average Thickness (nm)			
	Front Surface		Back Surface		Front Surface		Back Surface	
S4	3		3		429		477	
S5	20		20		422		434	
S6	30		30		335		372	
Sample (for 8-12 µm)	**Pressure (mTorr)**				**Average Thickness (nm)**			
	Front Surface		**Back Surface**		**Front Surface**		**Back Surface**	
	First	**Second**	**First**	**Second**	**First**	**Second**	**First**	**Second**
S10	3	20	3	20	429	422	429	422
S11	3	-	3	20	429	-	429	422
S12	3	-	3	-	314	-	1195	-

After growing thin films at film thicknesses determined according to wavelength ranges, single-surface and double-surface coating analyzes were performed. After the samples grown under the same pressure from both sides, we were tested from both sides. According to the order determined in the table, the first coating of the front surface is carried out under 3 mTorr, while the second surface coating is carried out under the determined pressure for both surfaces. For example, while ZnS thin films are produced on both the front surface and the back surface under a pressure of 3-3 mTorr, 3-20 mTorr indicates that the back surface is growth under 20 mTorr. After the samples were characterized under 3, 20 and 30 mTorr, they were enlarged as a single surface, then a double surface, and then as a multi-layer under different pressure. In this context, while XRD and AFM was based on 3, 20 and 30 mTorr single surface coatings in characterization processes, FTIR measurements was performed for all samples.

3. RESULTS AND DISCUSSION

a) Structural Analysis

Especially, ZnS is commonly obtained in two crystalline forms: (a) cubic structure and (b) hexagonal wurtzite structure. These different phases are a recognizable difference in their physical properties. The peak of 2θ ≈ 28.50° is observed for all of thin film samples. This angle, which corresponds to the (111) plane in the ZnS cubic structure, forms the (002) plane in the hexagonal structure. The (100) plane is also consists of hexagonal wurtzite structure. The formation of these two phases depends on the applied temperature. Cubic phase is formed at low temperatures, while hexagonal phase is formed at high temperatures.

The structure of ZnS thin films were analyzed by X-ray diffraction (XRD). Fig. 1 shows XRD patterns of the ZnS thin films obtained at different pressures on Ge. Ge substrates were oriented (111) plane and single crystalline form (JCPDS file no. 4-545)[24]. The XRD patterns of ZnS thin films were scanned in the scattering angle (2θ) ranging from 10° to 90°. Between these angle values, it was given a range of 25° and 30° to determine which of the crystal structure is formed. On the other hand, in Fig. 1, the present samples grown at various pressures had only (111) plane and exhibited a cubic structure (JCPDS file no. 5-566)[25]. The highest peak value of XRD measurement comes from Ge optical windows and the pressure change affects film quality. As seen in Figure 2, it is seen that the hexagonal wurtzite structure is formed with the prolongation of the coating time (JCPDS file no. 36-1450)[26, 27]. Similar X-ray diffraction peaks were obtained many works for ZnS thin film deposited by RF-sputtering [26, 27]

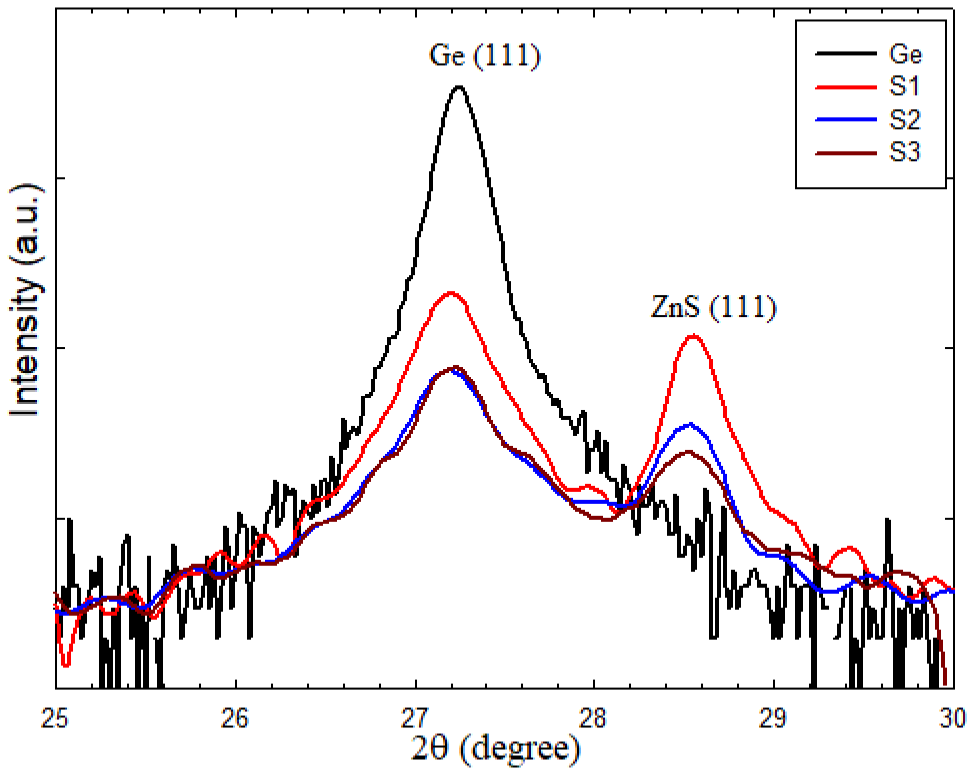

Figure 1. XRD patterns of ZnS films grown at different pressures

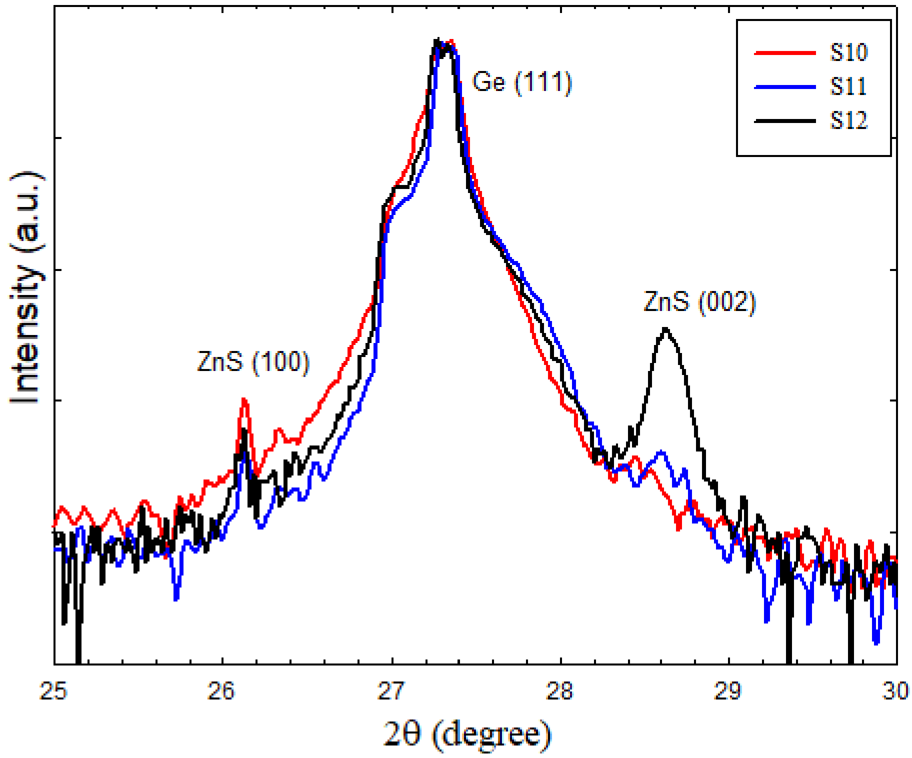

Figure 2. XRD patterns of ZnS films superimposed at different pressures

Figure 2. shows XRD patterns of superimposed ZnS thin films coating at different pressures. This indicated that the films were polycrystalline structures and that the planes were parallel to the substrate surface. For obtaining more structural information, the crystallite size of the prepared ZnS thin films were calculated from full width at half maximum (FWHM) of the diffraction peaks using the Debye-Scherrer equation [28];

$$D_{(hkl)} = \frac{k\lambda}{(\beta \cos \theta)} \tag{2}$$

where D is the crystallite size, k=0.9 is the crystallite shape factor, λ= 0.1540 nm is the wavelength of X-ray used for the diffraction measurements and β is the FWHM of the diffraction peaks at 2θ. The FWHM value of the film shows the disruption of the crystallinity, while the larger crystallite sizes indicate the improved crystallinity of the films [29]. FWHM values for ZnS thin films were measured by X-ray and shown in Table 3. XRD results shows better crystallinity for films produced under reduced pressures and the highest peak intensity clearly seen from the XRD spectra.

Table 3. The structural parameters of ZnS thin films

Sample	Average Thickness (nm)	β (degrees)	Crystallite Size by XRD (nm)
S1	429	0.261	32.83
S2	430	0.235	36,46
S3	421	0.228	37.59

b) Surface Analysis

The characterization of surface structures on a nanoscale is very important for the optoelectronic applications. Atomic force microscopy (AFM) is one of the several experimental techniques to study the surface properties of the deposited thin films [30]. AFM can be used to estimate crystallite grain size and surface roughness. AFM measurement was carried out to study the surfaces of Ge optical windows. Fig. 3 shows that two-dimensional (2D) and three-dimensional (3D) AFM images with 3 × 3 μm^2 scan area of the Ge optical windows with and without ZnS thin films.

We see a more homogeneous distribution in the scan with the presence of dark to indicate the presence of pockets or wells indicating the roughness of the thin films and also the absence of cracks on the surfaces of the layers, the same result was supported by Elidrissi. It can be seen in the Fig. 3 that the crystallinity of the films has been changed by different pressures of the sputtering system. Experimental results have shown that as the pressure increases, the crystal size values increase from 14.09 nm to 28.02 nm. The lowest roughness belongs to the sample grown under 3 mtorr pressure for films deposited in Ge optical windows. We can say that Ge is the smoothest substrate and has a size of the smallest grains. Surface roughness is all irregularities of the surface and micro-graphic character. This indicates that the rough nature of the thin layers of ZnS is caused by the growth mechanism of the technique of sputtering. Thanks to its roughness, this material allows light to be scattered rather than reflected at the interface; this allows high transmittance for almost all samples as shown in the subsequent analysis of optical spectra compared to the specular component.

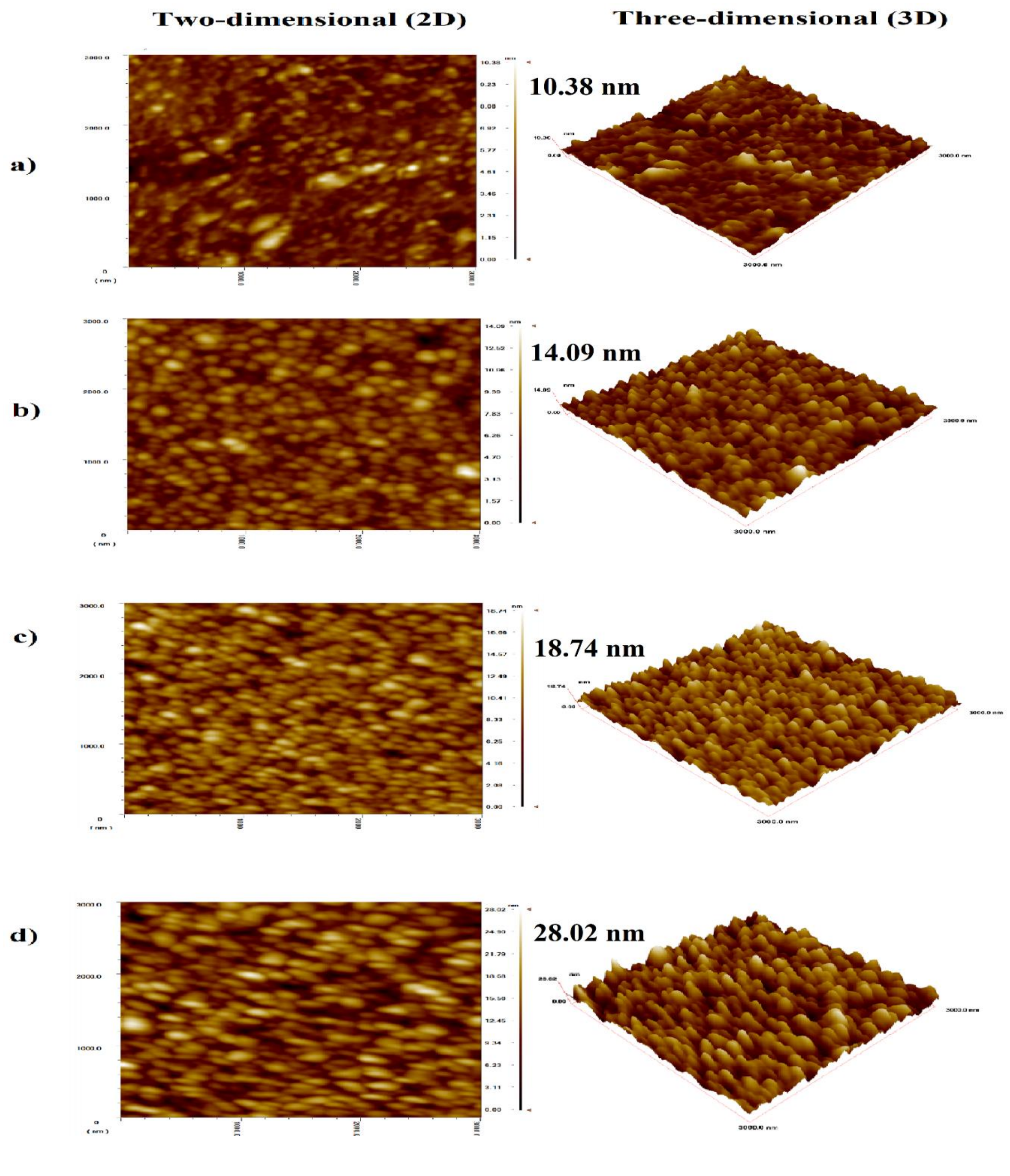

Figure 3. ZnS thin film AFM 2D and 3D images on Ge optical windows A) Ge without ZnS b) 3 mTorr Ge/ZnS c)20 mTorr Ge/ZnS d)30 mTorr Ge/ZnS

c) Optical Analysis

The optical properties of samples were analyzed using FTIR spectrometer. First of all, calibration was performed for FTIR device. ZnS thin film coated Ge optical windows are placed perpendicular to the beam direction. The transmission spectra for Ge optical windows are shown in Fig. 4-a, 4-b, 4-c and 4-d which was recorded at room temperature by the FTIR for wavelengths ranging from 2-20 µm. Figure 4-a and Figure 4-c are single-surface coated, while Figure 4-b and Figure 4-d are of samples double surface coated. While the maximum average transmittance, 67%, is observed for the film deposited one surface coating, double surface coating transmittance are observed 98% and 99%, respectively for 2-20 µm wavelength range. Growing ZnS atoms with different pressure parameters results in higher optical transmittance of the film. It can be seen that transmittance increases when the film thickness increases at superimposed thin films deposited. ZnS coated Ge optical windows can be observed to have increased optical transmission at certain wavelengths in the specified film thicknesses. Therefore, we note that the reflection curves are not interference; It is due to the multiple reflections of the two interference layers due to the importance of the roughness of thin films. Therefore, in our case this ZnS thin film can be applied as infrared imaging.

ZnS thin films were coated in soda lime glass using the same coating parameters to determine the refractive index. The UV-VIS transmission spectrum obtained glass, S1 and S10 samples and given in Fig. 5. Regarding the refractive index study as a function of wavelength variation in the UV- VIS region, it can be seen depending on the nature of the glass shown in Fig. 5. The graph indicate that the samples has a good optical transparency in visible and part of near infrared wavelength range with the average transmittance minimum of 60% and the maximum of 85%. The refractive index of ZnS was calculated as 2,18 with the help of envelope method [31, 32]. We note that the refractive index of the ZnS layer deposited on the glass is in agreement with reported references.

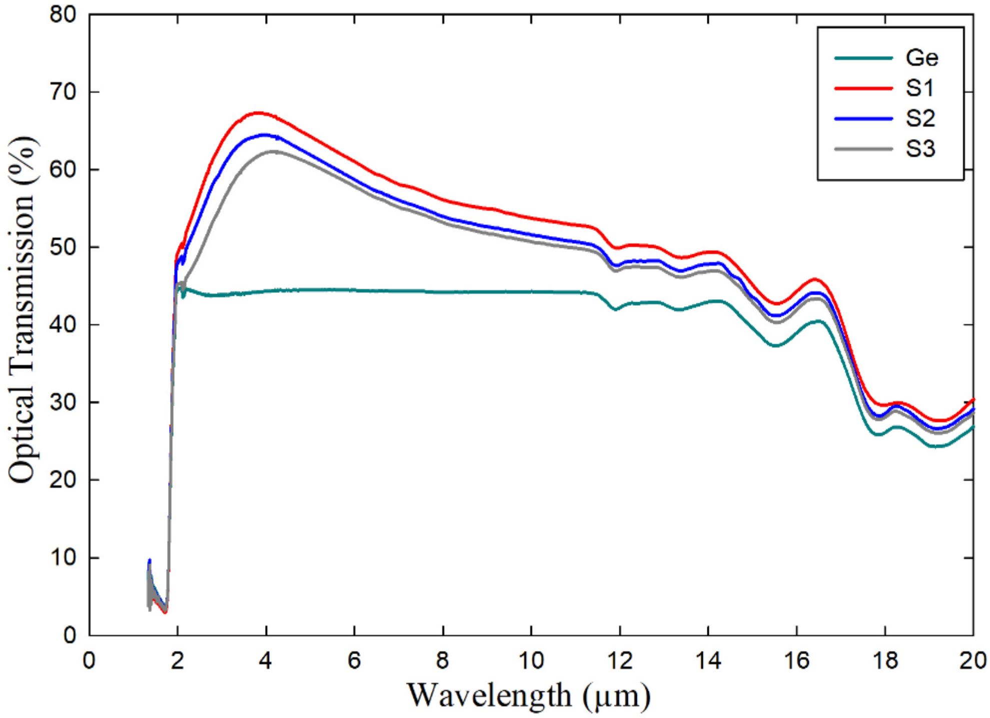

Figure 4- a. The optical transmission spectra of Ge optical windows with and without ZnS ARCs at different pressures

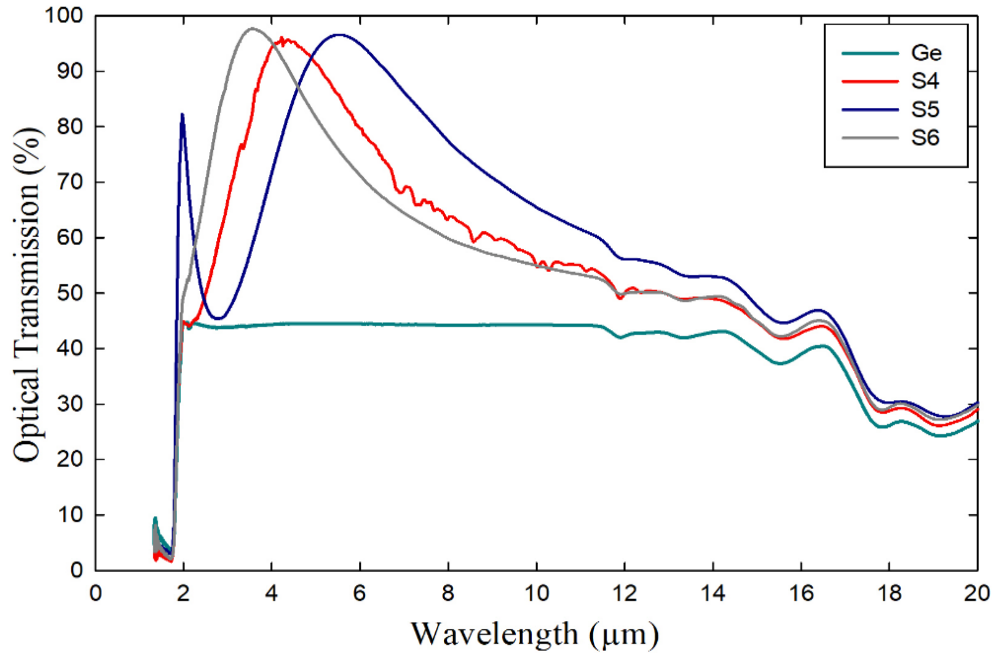

Figure 4- b. The optical transmission spectra of Ge optical windows coated on both surface at different pressures

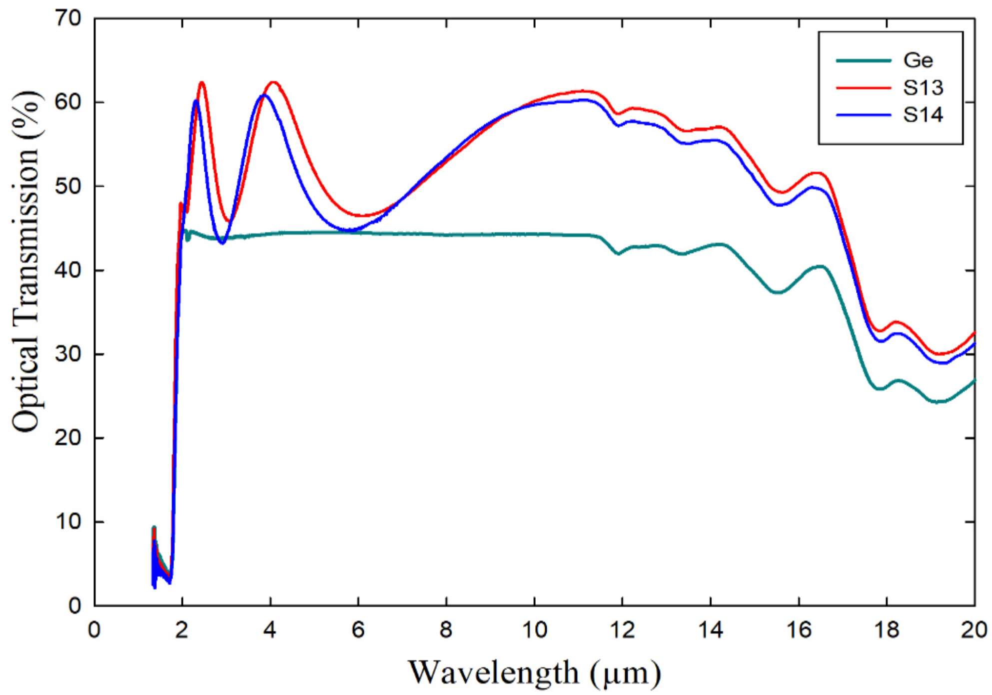

Figure 4- c. The optical transmission spectra of Ge optical windows with and without ZnS ARCs for 8 -12 µm at different pressures

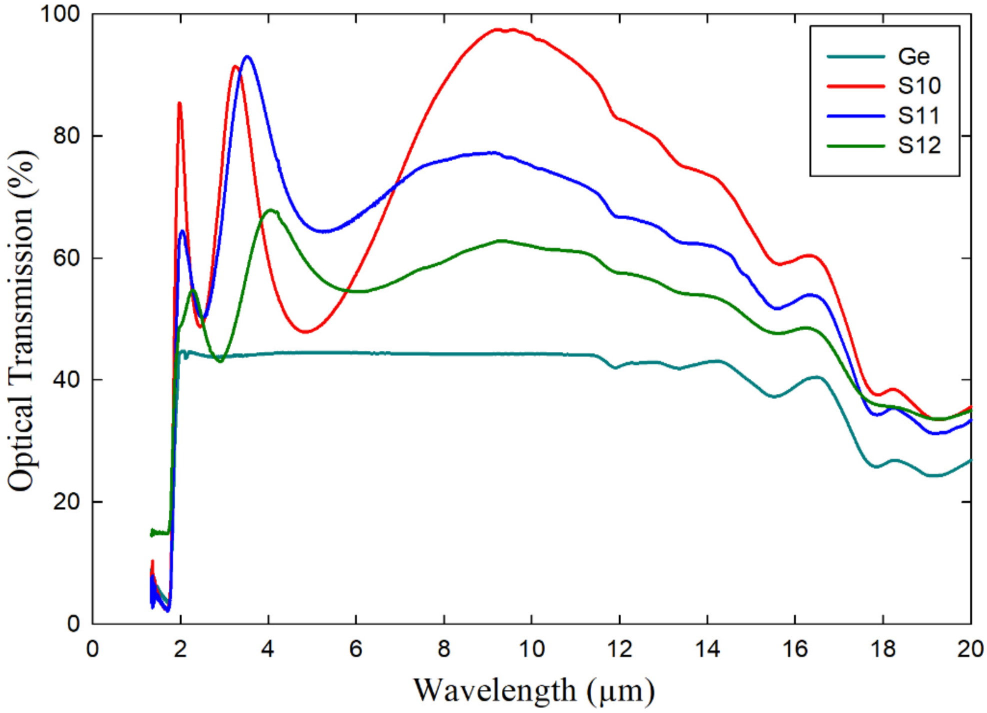

Figure 4- d. The optical transmission spectra of Ge optical windows coated on both surface at different pressures for 8 -12 μm.

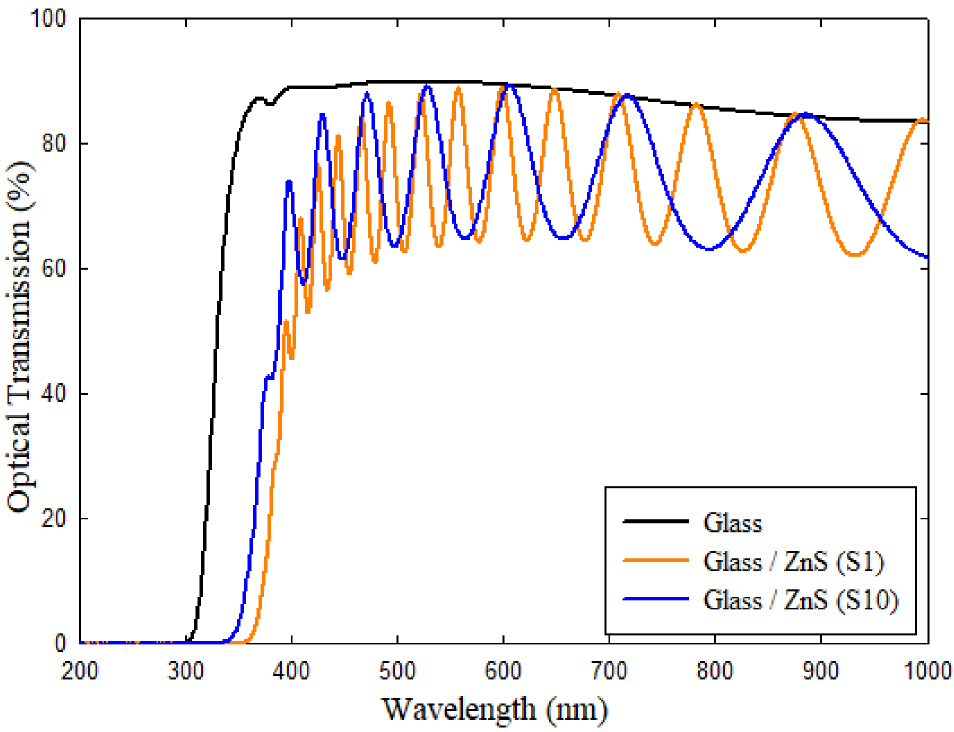

Figure 5. The optical transmission spectra of ZnS thin film on glass

4. CONCLUSION

In summary, ZnS antireflection films were successfully deposited on Ge optical windows and soda lime glass at different pressures by RF magnetron sputtering. It was found that the deposited ZnS thin films exhibited a strong XRD peak at around 28.50 degree with an orientation of the (111) plane. X-ray diffraction analysis has also revealed a change in the thin film structure from cubic to hexagonal. AFM measurements showed that the surface roughness and grain sizes of the films increased as the pressure decreased. The FTIR results indicate that the IR transmission increases by about 26% on surfaces of the Ge by deposition of single layer ZnS ARC and the maximum is almost 99% in the 2-14 nm wavelength range using double layer coating. Using envelope method, Refractive index was determined. UV - Vis spectra showed that ZnS thin films has a good transmission. The peak position of the maximum in the transmittance spectra for optical windows can be shifted to the wanted wavelength by changing the optical thickness of the coating.

SIMILARTY RATE: 16%

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